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(54) **Polyamide resins.**

(57) Polyamides containing free amino groups and suitable for use as curing agents for polyepoxy compounds are derived from (a) a polybasic acid component comprising polymeric fatty acid together with from 10 to 90 mole %, based on the total acid component, of one or more aromatic dicarboxylic acids containing two carboxylic acid groups and one benzene ring, each carboxylic acid group being directly linked to a benzene ring, and (b) a polyamine component containing at least 50 mole % of one or more aliphatic polyamines containing at least three amino groups per molecule.

Cured resinous composition may be prepared by reacting the polyamides with polyepoxy compounds and curable composition contain the polyamides together with polyepoxy compounds.

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Polyamide resins

This invention is concerned with improvements in and relating to polyamide resins. More particularly, the invention is concerned with polyamide resins containing
5 free (non-amidified) amino groups and which are suitable for use as curing agents for polyepoxy compounds (so-called "epoxy resins").

The use of polyamide resins containing free amino groups as curing agents for polyepoxy compounds is well
10 established. Thus such polyamides derived from the polycondensation of polymeric fatty acids and aliphatic polyamines are disclosed in United States Patent No. 2430940 and compositions comprising polyepoxy compounds together with such polyamides are disclosed in United
15 States Patent No. 2705223 and British Patent Specification No. 726570. Polyamide curing agents derived from polymeric fatty acids and aliphatic polyamines are commercially available under the trade name "Versamid", being manufactured in the United
20 Kingdom by Cray Valley Products Limited and in the United States of America by Henkel Corporation of America (formerly General Mills).

Polyamide curing agents react with polyepoxy compounds to form cured systems by reaction of free amino groups of the polyamide with epoxy groups of the polyepoxy compound, leading to gradual cross-linking and insolubilisation of the system. At ambient temperature, reaction takes place over a period of time depending on the nature of the polyamide curing agent and the polyepoxide compound and the ratio of polyamide to polyepoxy compound. The application of heat accelerates the reaction.

Polyepoxide compound/polyamide curing agent systems are widely used in the surface coatings art. The outstanding toughness, chemical resistance and corrosion resistance of coatings based on such systems coupled with their excellent adhesion to a variety of substrates make them ideal for heavy duty maintenance coatings.

However, when used in combination with some types of epoxy resins, preferably available polyamides are less than satisfactory. Thus, drying times may be extremely long and surface defects such as residual tackiness, blooming, cissing or rivelling may be apparent, especially under adverse conditions such as low temperature and/or high humidity. In order to overcome such problems it has been proposed to pre-age the polyamide/epoxy resin mix before use or to use a

polyamide/epoxy resin adduct in place of the polyamide curing agent; as disclosed, for example, in British Patent No. 988 484.

5 It has now been found, in accordance with the present invention, that certain polyamides derived from certain aromatic polybasic carboxylic acids and polymeric fatty acids are useful curing agents for polyepoxy compounds and possess, inter alia, the advantages that they can give systems which have shorter
10 drying times than the polyamide curing agents discussed above, and give products free from surface defects as discussed above.

According to the invention, therefore, there is provided a polyamide containing free amino groups and
15 suitable for use as a curing agent for polyepoxy compounds which polyamide is derived from

- (a) a polybasic acid component containing a polymeric fatty acid together with from 10 to 90 mole %, preferably from 20 to 80 mole %, based on the total
20 of the polybasic acid component, of one or more aromatic dicarboxylic acids; and
- (b) a polyamine component containing at least 50 mole % of one or more aliphatic polyamines containing at least three amino groups per molecule

Polymeric fatty acids for use in accordance with the invention are well-known and are obtained by the polymerization of unsaturated long chain fatty acids as described, for example, in "The Chemistry of Organic Film Formers", D.H. Solomon, Krieger 1977, at pages 69 and 70. The polymerization products consist largely of dimers (and hence are often referred to as "dimer acids") together with smaller amounts of trimers and higher oligomers. Polymeric fatty acids (dimer acids) are commercially available, for example under the trade names "Craymer" (Cray Valley Products Ltd.) and "Empol/Pripol" (Unichema).

Aromatic dicarboxylic acids for use in accordance with the invention are those containing two carboxylic acid groups and at least one benzene ring, each carboxylic acid group being directly linked to a benzene ring. Where the acid contains two benzene rings these may be directly linked to each other or via the intermediary of a short length linking group such as an oxygen atom or methylene group. Particular examples of aromatic dicarboxylic acids which may be used include isophthalic acid, terephthalic acid, diphenic acid (diphenyl 2,2'-dicarboxylic acid), and diphenyl ether-4,4'-dicarboxylic acid.

In addition to the polymeric fatty acid and aromatic dicarboxylic acids, the acid component may contain minor

amounts of monocarboxylic acids to control the molecular weight of the polyamide. Examples of such mono-functional acids are monocarboxylic aliphatic acids such as acetic acid, propionic acid, isobutyric acid and long chain fatty acids; and aromatic monocarboxylic acids such as benzoic acid and butyl benzoic acid.

The acid component may also contain aliphatic dicarboxylic acids such as adipic acid, pimelic acid, azelaic acid, sebacid acid, dodecane dioic acid and West
 10 Vacco di-acid (a C_{21} dicarboxylic acid prepared by the addition of ascrylic acid to conjugated linoleic acid). In addition, the acid component may contain, minor amounts of anhydrides such as maleinised fatty acids, phthalic anhydride, trimellitic anhydride, pyromellitic
 15 di-anhydride and do-decenyl succinic anhydride.

In any event, however, the acid component should contain at least 10 mole % of polymeric fatty acid, preferably at least 30 mole % thereof.

Preferred aliphatic polyamines for use in the
 20 invention are those of the formula:



in which R is an alkylene radical, especially a

methylene radical, and n is an integer of from 1 to 6. Examples of such amines include diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene-hexamine, di-1,3-propane triamine, tri-1, 3-propane tetramine, di-1,2-propane triamine and the like. The polyamine component may consist only such of such polyamines or may comprise other polyamines, for example alpha-omega aliphatic diamines (such as ethylene diamine, propylene diamine, tetramethylene diamine and hexamethylene diamine); and cycloaliphatic diamines such as 1,4-diamino-methyl- cyclohexane and isophorone diamine.

The amine compound may also contain, in order to control molecular weight, minor amounts of monoamines such as fatty amines, propylamine and butylamine.

The polyamides of the invention are produced by polycondensation of an appropriate polybasic acid component with an appropriate polyamine component. The polycondensation is carried out under conditions conventional for the production of polyamides, for example at temperatures of from 200 to 280°C, preferably from 230 to 250°C, and under conditions such that water evolved during the course of the polycondensation may be removed from the reaction mixture. (In this connection it may be noted that in some cases the polybasic acid

component may comprise, at least in part, lower alkyl esters of the acids from which the polyamide is derived. In this case polycondensation should, of course, be carried out under conditions such that the
5 lower alcohol formed during the course of the condensation is removed from the reaction medium. As will be appreciated, in principle a polyamide derived from an ester of an polycarboxylic acid is the same as one derived from the acid per se.

10 The polycondensation reaction may be carried out by charging all the ingredients to a suitable reactor or may be carried out by adding the reactants in stages to the reactor.

The polycondensation will generally be carried out
15 using an excess of amino groups over carboxylic acid groups and the resulting polyamide, the polyamide of the invention, suitably has an amine value of from 100-400 mgKOH/g, preferably from 150-350 mgKOH/g. Preferably the acid value of the polyamide is from 0 - 20 mgKOH/g.

20 The polyamides of the invention range from balsam-like materials to hard resinous materials having melting points in the range of 60-150°C depending on the amount of aromatic acid employed and the nature and amount of amine employed. In general, the lower melting point

products are soluble in solvents such as xylol whilst the higher melting point products display solubility in aliphatic alcohols, such as ethanol, propanol or butanol, or mixtures thereof with xylol. Dissolution of
5 the polyamide in the solvent may be accomplished by either cold churning or by refluxing the resin/solvent mixture.

As noted above, the polyamides of the invention are suitable for use as curing agents for polyepoxy
10 compounds.

Thus, a further embodiment of the invention provides a process for the production of a cured resinous product which comprises reacting a polyamide in accordance with the invention with a polyepoxy compound. Further, the
15 invention provides curable compositions comprising polyamide of the invention together with a polyepoxide compound. In this latter connection it will, of course, be understood that such compositions will tend to react and will hence be marketed in the form of two-part
20 packs, one part containing the curing agent (polyamide resin) and the other containing the polyepoxide compound.

The polyamides of the invention may be used to cure a wide variety of polyepoxy compounds. Thus, for a general review of polyepoxy compounds reference may be

made to "Handbook of Epoxy Resins", Lee and Neville,
McGraw-Hill, 1967, Chapters 1-3 and "Encyclopedia of
Polymer Science and Technology", Mark and Gaylord,
Interscience Publishers, 1967, pages 209-270 - "Epoxy
5 Resins".

Thus by way of example the polyamide curing agents
of the invention may be used in the curing of polyepoxy
compounds derived from bisphenols, especially
bisphenol-A, such as those sold under the trade names
10 Epikote 828 and 1001 (Shell) and D.E.R. 334 (Dow).
Similarly the polyamides may be used to cure
hydrogenated polyepoxy compounds derived from bisphenols
such as that sold under the trade name "DRH 152"
(Shell). Other polyepoxy compounds which may be cured
15 include flexible polyepoxy compounds (such as that sold
under the trade name Epikote 872); Hydantoin based
polyepoxy compounds (such as that sold under the trade
name MS6064 by Ciba-Geigy); Epoxy acrylics (such as
those sold under the trade name Epirez 5027 and 50727 by
20 Celanese); polyepoxides derived from polyols [e.g.
glycerol triglycidyl ether as sold under the trade name
G-1701 (Grilonit) and Sorbitol polyglycidyl ether sold
under the trade name EX 612 (Nagase)]; and epoxy
novolaks (such as that sold under the trade name DEN 431
25 by Dow).

In order that the invention may be well understood the following examples are given by way of illustration only.

EXAMPLE 1

5 (Comparative Example)

Tall oil fatty acids (168g) and dimerised fatty acids (168g) were charged to a 5 litre flask fitted with a 5 litre flask fitted with an anchor stirrer, nitrogen inlet and thermometer. The temperature was raised to 100°C and adipic acid (394g) added, after which the batch temperature was raised to 150°C. Triethylene tetramine (960g) was added over a period of 30 minutes, the temperature being maintained at 150°C. At the end of the addition, the temperature was raised to 240°C and the batch held at this temperature for a period of four hours, water of reaction being allowed to escape from the flask.

The batch was cooled to 200°C and vacuum applied to remove any water remaining. After cooling to 140°C the batch was thinned to approximately 60% non-volatiles in xylol.

The product had an amine value of 220 mgKOH/g.

EXAMPLE 2

The procedure of Example 1 was repeated using isophthalic acid (448g) in place of adipic acid.

5 The product had an amine value of 215 mgKOH/g.

EXAMPLE 3

Dimerised fatty acids (112g) and isophthalic acid (132.8g) were charged to a 1 litre flask and heated to 130°C. Triethylene tetramine (160g) was added over a
10 period of 15 minutes, after which the temperature was raised to 240°C. After a period of three hours at 240°C the batch was cooled to 220C and 25" vacuum applied for a period of one hour. The high melting point resin obtained was cooled to approximately 160°C at which
15 point it was thinned to approximately 60% solids by the slow addition of butanol.

The resin had an amine value of 350 mgKOH/g.

EXAMPLE 4

The procedure of Example 2 was repeated using

dimethyl terephthalate (524g) in place of isophthalic acid.

The product had an amine value of 225mgKOH/g.

EXAMPLE 5

5 A polyamide was made following the procedure of Example 3 using tall oil fatty acids (44g) dimerised fatty acids (634g), isophthalic acid (83g) and 44' diphenyl ether di-carboxylic acid (129g) and tetraethylene pentamine (456g).

10 The product was soluble in xylol and had an amine value of 300mKOH/g.

EXAMPLE 6

15 A polyamide was made following the procedure of Example 3 using dimerised fatty acids (336g), isophthalic acid (33.2g), diphenic acid (48.4g) and diethylene triamine (144g).

The product was soluble in xylol and had an amine value of 208mKOH/g.

EXAMPLE 7

The procedure of Example 3 was repeated using dimerised fatty acids (112g), azelaic acid (37.6g), isophthalic acid (99.6g) and diethylene triamine (105g). The product had a melting point of 100°C and an amine value of 195mgKOH/g and was soluble in butanol.

EXAMPLE 8

A curing agent was made following the procedure of Example 3 using tall oil fatty acids (56g), dimerised fatty acids (224g), isophthalic acid (83g) and diethylene triamine (103g).

The product had an amine value of 120mgKOH/m and an acid value of 8.0 mgKOH/g.

EXAMPLE 9

The procedure of Example 3 was repeated using dimerised fatty acids (168g), isophthalic acid (116.4g), ethylene diamine (12g), and diethylene triamine (82.4g).

The solid resin had an amine value of 128mgKOH/g, an acid value of 10.6 mgKOH/g and a melting point of 110°C.

EXAMPLE 10(Comparative)

A polyamide was made according to Example 7 of British Patent Specification No. 789,108 from dimethyl
5 terephthalate (97g) and triethylene tetramine (73g).
The product was thinned to 70% non-volatile in butanol and had an amine value of 270 mgKOH/g.

EXAMPLE 11(Comparative)

10 A curing agent was made according to the procedure of Example 3 from dimerised fatty acids (494g),
isophthalic acid (16.6g) and triethylene tetramine (209g).

The product had an amine value of 215 mgKOH/g.

15 Solutions of the polyamides of Examples 1-9 were made in the appropriate solvents, either xylol or butanol or mixtures thereof. In addition to Example 1 a solution of a commercially available polyamide based on
dimerised fatty acids (Versamid 115X) was used as a
20 comparative example.

These solutions were then used to cure various polyepoxy compounds, mixing ratios were determined from the amine value of the polyamide and the oxirane value of the polyepoxy compound, a slight excess (5%) of the epoxy compound being used. After mixing the solutions were each thinned to 3 poise with a 3:1 xylol/butanol mixture, and applied to glass panels without pre-ageing using an 0.004" applicator. The results obtained are shown in Table 1.

Table II compares the properties of coatings based on curing agents of the invention with those of the prior art. White gloss finishes were prepared using Epikote 828 as the co-reactant. They were pigmented with rutile titanium dioxide RCR 2 to give a pigment:binder ratio of 0.8:1. They were thinned to give a viscosity of 4.0 poise with butanol and applied without preageing to burnished steel panels to give a dry film thickness of the order of 30 microns. Tests were carried out after 7 days air dry.

TABLE I - CURE WITH EPOXY RESINS

CURING AGENT	EPOXY RESINS					
	Epikote 828	Epikote 828(1)	D.E.R. 334	D.R.H. 151	MS 6064	EX 612
Vers. 115 COMPARATIVE (based on dimer- ised fatty acids).	Greasy film Cissing and crawling. Trough dry 15 hours	Greasy opaque film. Cissing and crawling. Touch dry 24 hours	Greasy film. Cissing and crawling. Touch dry 15 hours	Extensive cissing and crawling. Non drying	Extensive cissing and crawling. Non drying	Greasy rivelled films. Residual Tack.
	Greasy film Cissing and crawling. Trough dry 15 hours	Greasy opaque film. Cissing and crawling. Touch dry 24 hours	Greasy film. Cissing and crawling. Touch dry 15 hours	Extensive cissing and crawling. Non drying	Extensive cissing and crawling. Non drying	Greasy rivelled films. Residual Tack.
Examples 2-9 (products of in vention containing aromatic di-acids).	Touch dry 0.5-3 hours	Touch dry 2-8 hours	Clear non greasy films Free of imperfections Touch dry 0.5-3 hours	Touch dry 0.5-5 hours	Touch dry 0.5-5 hours	Touch dry 0-5-5 hours
	Touch dry 0.5-3 hours	Touch dry 2-8 hours	Clear non greasy films Free of imperfections Touch dry 0.5-3 hours	Touch dry 0.5-5 hours	Touch dry 0.5-5 hours	Touch dry 0-5-5 hours

1. Films applied at 0°C and 95% R.H. Other films applied at 21°C and 40% R.H.

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TABLE II - CURE WITH EPIKOTE 828

CURING AGENT	VERSAMID 115	EXAMPLE 11	EXAMPLE 2	EXAMPLE 3	EXAMPLE 10
Isophthalic acid %	0	10	50	80	100
Amine value mgKOH/g	220	215	215	350	270
Curing agent/Ep 828 ratio	57/43	58/42	58/42	46/54	52/48
Film appearance	Incompatible Extremely greasy Extensive cissing	Slightly greasy	Fully satisfactory		Slightly greasy
Gloss	-	89	93	90	33
	-	95	97	96	75
Bend	-	1	1	1	1
Reverse impact	-	1.25	1.25	-	-
	-	2.5	2.5	1.25	1.25
Slow indent	-	8.0	7.8	6.9	2.0
Crosshatch adhesion	-	100	95	95	90

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CLAIMS:-

1. A polyamide containing free amino groups and suitable for use as a curing agent for polyepoxy compounds, characterized in that the polyamide is
5 derived from (a) a polybasic acid component comprising polymeric fatty acids together with from 10 to 90 mole %, based on the acid component of one or more aromatic dicarboxylic acids containing two carboxylic acid groups and at least one benzene ring, each carboxylic acid group
10 being directly linked to a benzene ring, and (b) a polyamine component containing at least 50 mole % of one or more aliphatic polyamines containing at least three amino groups per molecule.
2. A polyamide as claimed in claim 1, characterized in
15 that the aromatic dicarboxylic acid is isophthalic acid, terephthalic acid, diphenic acid or diphenyl ether-4,4'-dicarboxylic acid.
3. A polyamide as claimed in claim 1 or claim 2, characterized in that the polybasic acid component also
20 contains up to 50 mole % of one or more of aliphatic dicarboxylic acids.

4. A polyamide as claimed in any one of the preceding claims, characterized in that the aliphatic polyamide has the formula:



5 in which R is an alkylene radical (especially a methylene or ethylene radical) and n is an integer of from 1 to 6.

5. A polyamide as claimed in any one of the preceding claims characterized in that it has an amine value of
10 from 100 to 400 mgKOH/mg.

6. A polyamide as claimed in any one of the preceding claims characterized in that it has an acid value of from 0 to 20 mgKOH/g.

7. A process for the production of a cured resinous
15 product by reacting a polyamide with a polyepoxy compound characterized in that the polyamide is a polyamide as claimed in any one of the preceding claims.

8. A curable composition comprising a polyamide together with a polyepoxy compound, characterized in
20 that the polyamide is a polyamide as claimed in any one of claims 1 - 6.